160 ml with petroleum ether (bp 30–60°) and 5.2 g (0.066 mol) of pyridine was added with stirring. The reaction mixture was then filtered to remove pyridinium salts and the filtrate was evaporated at 100-mm pressure to give 3.7 g (95% yield) of **3a**.

Thermolysis of 3a and 3b.—A neat sample of 3,3-dimethyl-thietane-2,4-dione (**3a**) was heated at 145° for 1.5 hr (evolution of gas began at 130°). On cooling, a white, crystalline solid formed. A sample sublimed at atmospheric pressure gave mp 113–115°. The melting point was not depressed upon admixture with 2,2,4,4-tetramethylcyclobutane-1,4-dione (obtained from Aldrich Chemical Co). Nmr (singlet at 1.31 ppm) confirmed the identity.

A neat sample of 3,3-diethylthietane-2,4-dione (**3b**) was placed in a short-path microdistillation apparatus equipped with a Dry Ice cooled receiver and heated under nitrogen, at atmospheric pressure from room temperature to 170° over a 30-min period. Gas evolution was apparent at 145°. The ir spectrum of the pale yellow liquid which distilled into the receiver showed a strong band at 2100 cm^{-1} (diethylketene[8]) and a weak absorption for starting material at 1820 cm^{-1}. Gc analysis indicated the presence of 95% diethylketene and 5% starting material.

Registry No.—**1a**, 34803-94-6; **1b**, 34803-95-7; **1c**, 34803-96-8; **2a**, 34803-97-9; **2b**, 34803-98-0; **2c**, 34803-99-1; **3a**, 34804-00-7; **3b**, 34804-01-8; **3c**, 34804-02-9.
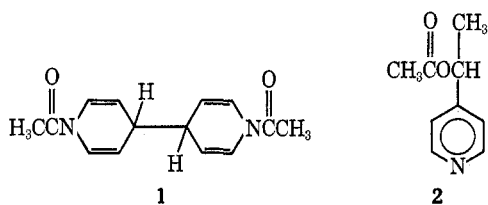

Zinc Reduction of 4-Methylpyridine in Acetic Anhydride

S. L. Johnson* and S. A. Anthony

Department of Biochemistry, School of Medicine, University of Pittsburgh, Pittsburgh, Pennsylvania 15213, and Department of Chemistry, Vassar College, Poughkeepsie, New York 12601
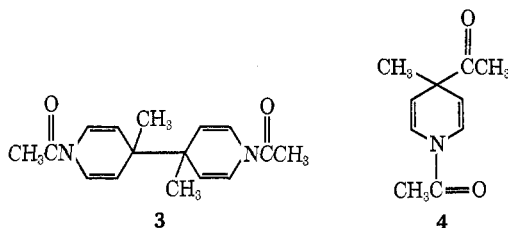
Mild treatment of pyridine with zinc and acetic anhydride results in the formation of 1,1′-diacetyl-1,1′,4,4′-tetrahydrobipyridine (**1**).[1,2] Pyrolysis of **1** at

1　　　　　　**2**

2 mm and 250–275° results in the formation of 1-(4-pyridyl)ethyl acetate[3] (**2**).

The present work is an attempt to prepare 1,1′-diacetyl-4,4′-dimethyl-1,1′,4,4′-tetrahydrodipyridine (**3**)

3　　　　　　**4**

by applying the conditions of the zinc reduction to 4-methylpyridine. We did not obtain the expected prod-

uct **3**, but instead we obtained 1,4-diacetyl-4-methyl-1,4-dihydropyridine (**4**).

The zinc reduction product of 4-methylpyridine and acetic anhydride was shown not to be structure **3** on the basis of molecular weight and elemental analysis. The assignment of **4** as the structure is based upon the nmr spectrum. Low-field protons assigned to H_2 and H_6 occur as a double doublet at δ 7.28 and 6.77 (J = 7.5 cps) with an area of 1 for each doublet. H_3 and H_5 occur as a single doublet at δ 4.97 (J = 7.5 cps), with an area of 2. Two methyl signals (area of 3) occur as sharp singlets at δ 2.27 and 2.22 and are assigned as the acetyl signals. A third methyl (area of 3) occurs as a singlet at δ 1.27 and is assigned as the 4-methyl group of **4**. The nmr spectrum of **4** in CDCl$_3$ is very similar to that of **1** in CDCl$_3$, in which the 2,2′ and 6,6′ protons occur as a double doublet at δ 7.23 and 6.68 with coupling constant of 11 cps, and the 3,3′,5,5′ protons of **1** occur as a multiplet at δ 4.92.[4] Due to their *N*-acetyl groups the nmr absorptions of the ring protons of **1** and **4** occur at much lower field than the corresponding absorptions of other dihydropyridines. Examples are the chemical shifts for 1-phenyl-1,4-dihydropyridine[5] and 1,4,4-trimethyl-1,4-dihydropyridine,[6] which occur at δ 6.27 and 5.51 for the 2,6 protons and at δ 4.53 and 4.11 for the 3,5 protons.

The infrared spectrum of **4** displays very strong bands at 1670 and 1692 cm^{-1}. The 1670-cm^{-1} band is attributed to the >C=C< by analogy with other dihydropyridine systems.[3,6,7] The 1692 and 1624-cm^{-1} bands are due to carbonyl stretching of **4** and **1**.

The ultraviolet spectrum of **4** in water, 1 *M* HCl, 0.1 *M* HCl, and 0.1 *M* NaOH occurs at 2530 Å with an extinction coefficient of 1.9 × 10^4 M^{-1} cm^{-1}. An overnight treatment of **4** with 0.1–1 *M* HCl or 0.1–1 *M* NaOH completely abolishes its ultraviolet absorbance, indicating hydrolytic instability of **4**. The ultraviolet absorbance of **4** is similar to that of **1**[4] (λ_{max} 2630 Å, ϵ_{max} 2.4 × 10^4 M^{-1} cm^{-1}).

The failure to obtain **3** upon treatment with zinc and acetic anhydride can be ascribed to the instability of bipyridines which are hindered at the 4,4′ positions. The early work of Mumm[8,9] and Emmert[10] clearly indicates that compounds **5–7**, formed by reduction of
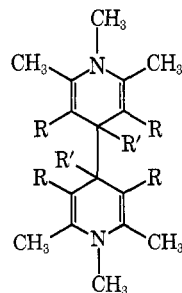
5, R = CO$_2$Et; R′ = *i*-Bu
6, R = R′ = CH$_3$
7, R = H; R′ = CH$_3$

(1) O. Dimroth and F. Frister, *Ber.*, **55**, 1223 (1922).
(2) O. Dimroth and R. Heene, *ibid.*, **54**, 2934 (1921).
(3) A. T. Nielsen, D. W. Moore, J. H. Mazur, and K. H. Berry, *J. Org. Chem.*, **29**, 2898 (1964).
(4) A. T. Nielsen, D. W. Moore, G. M. Muha, and K. H. Berry, *ibid.*, **29**, 2175 (1964).
(5) M. Saunders and E. H. Gold, *ibid.*, **27**, 1439 (1962).
(6) E. M. Kosower and T. S. Sorensen, *ibid.*, **27**, 3764 (1962).
(7) R. L. Frank, F. Pelletier, and F. W. Starks, *J. Amer. Chem. Soc.*, **70**, 1767 (1948).
(8) O. Mumm and H. Ludwig, *Ber.*, **59B**, 1605 (1926).
(9) O. Mumm, O. Rodel, and H. Ludwig, *ibid.*, **57B**, 865 (1924).
(10) B. Emmert and O. Werb, *ibid.*, **55B**, 1352 (1922).

the corresponding pyridinium ions with sodium amalgam, are unstable upon storage and form compounds of lower molecular weight. The instability of **1** to heating with the resultant formation of **2**,[3] presumably by a disproportionation reaction shown in eq 1, strongly suggests that **3**, if formed, would disproportionate to **4** *via* **8** as shown in eq 2.

$$(1)$$

$$(2)$$
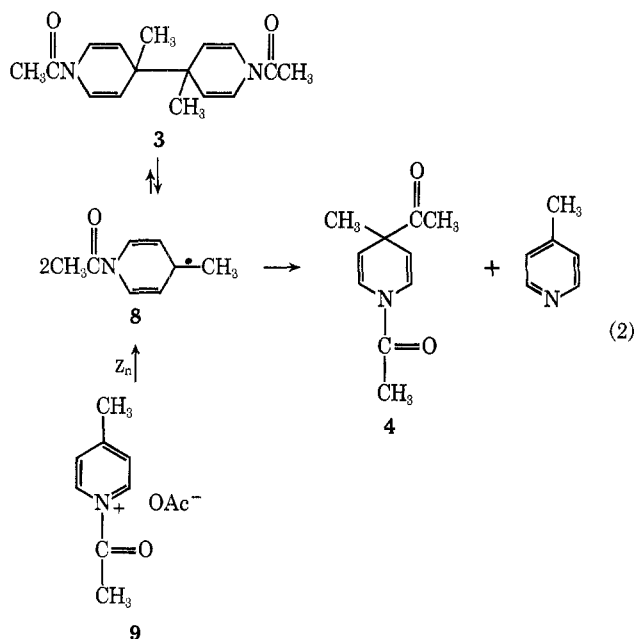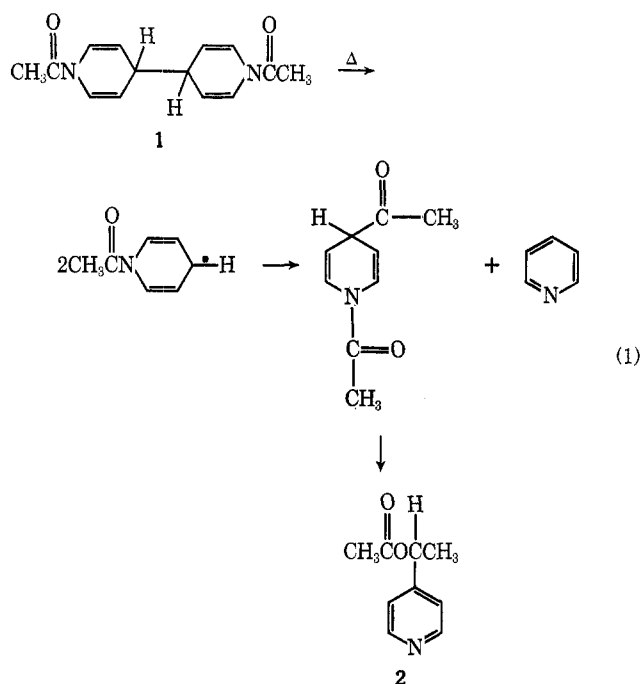
Experimental Section

Materials.—4-Methylpyridine, acetic anhydride, and 40 mesh zinc were reagent grade materials from Fisher Scientific Co.

Preparation of 4.—The procedure of Dimroth and Heene[2] was used with the substitution of 4-methylpyridine for pyridine. 4-Methylpyridine (50 ml) and 200 ml of acetic anhydride were mixed together in an erlenmeyer flask. After the addition of 50 g of zinc the reaction mixture was agitated in the stoppered flask with a magnetic stirrer for 16 hr–14 days at 30–35°. The only color change which was noticeable was a yellowing of the reaction mixture. The early precipitate formed was very soluble in water and is Zn(OAc)₂ based upon its nmr spectrum in D₂O and the presence of a residue upon burning. The flask and its contents

were treated with 200 ml of water and heated to 85° in a water bath in order to dissolve the precipitate. The zinc was separated by filtration using hot acetic anhydride to wash the filter. The filtrate was refrigerated overnight and crystals of **4** were collected and recrystallized from methanol, mp 80–81°. A yield of 15–17% was obtained independent of the time of work-up. *Anal.* Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.81; O, 17.85. Found: C, 67.02; H, 7.44; N, 7.77; O, 17.77 (by difference). The molecular weight of **4** was determined in chloroform by vapor phase osmometry to be 181, agreeing well with the value of 179 calculated for $C_{10}H_{13}NO_2$.

Physical Measurements.—The spectral determination of **4** was made with a Beckman IR-4 infrared spectrometer, a Cary 14 ultraviolet–visible spectrophotometer, and a Varian A-60 nuclear magnetic resonance spectrometer.

The Reaction of Dilithium Cyclooctatetraenide with Phosgene. Preparation of Bicyclo[4.2.1]nona-2,4,7-trien-9-one[1]

M. SAKAI,*[2] R. F. CHILDS, AND S. WINSTEIN[3]

Department of Chemistry, University of California at Los Angeles, Los Angeles, California 90024

Although the chemistry of bicyclo[4.2.1]nonatrienols has been explored to a considerable extent,[4] the corresponding parent ketone, bicyclo[4.2.1]nona-2,4,7-trien-9-one (**1**), has not been described. This system has been synthesized by the reaction of dilithium cyclooctatetraenide with phosgene.[5] Cyclooctatetraene was converted into its dianion, which was treated with excess ethereal phosgene at −40° and then quenched with water. The resulting mixture, containing two main products, was subjected to tlc. The component of shorter R_f was formed in about 19% yield and established to be the desired **1** on the basis of the mass spectrum [parent peak, m/e 132 ($C_9H_8O^+$)] and nmr spectrum [τ 4.29 (6 H) and saturated bridgehead proton absorptions centered at τ 7.09 (2 H)]. The ir spectrum shows weak absorption at 3045 cm⁻¹ (olefinic C–H) and strong absorption at 1755 cm⁻¹ (C=O, similar to that of bridgehead ketones[6]). The addition of CH₃MgI to **1** resulted in the formation of one alcohol, indistinguishable from an authentic sample of *syn*-9-hydroxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (**2**)[4a] on the basis of vpc comparison on two columns and nmr and ir spectral comparison. The component of longer R_f, formed in 22% yield, was 3-chloroindene (**3**).[7]

(1) Part of this work was described in a Communication to the Editor: M. Sakai, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4452 (1970).

(2) Address correspondence to this author at Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

(3) Deceased Nov 23, 1969.

(4) (a) T. S. Cantrell and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 5868 (1967); (b) L. G. Cannell, *Tetrahedron Lett.*, 5947 (1966); (c) A. S. Kende and T. L. Bogard, *ibid.*, 3383 (1967); (d) M. Sakai and S. Winstein, unpublished results.

(5) After the present method had been perfected, we learned that Professor H. Shechter and coworkers made **1** by the reaction of dilithium cyclooctatetraenide with dimethylcarbamoyl chloride.

(6) (a) C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, **82**, 4067 (1960); (b) H. K. Hall, Jr., and R. Zhinden, *ibid.*, **80**, 6428 (1958); (c) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964); (d) C. F. H. Allan, T. Davis, D. W. Stewart, and J. A. VanAllan, *ibid.*, **20**, 306 (1955).

(7) E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 3337 (1955).